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## EFFECT OF ADDITIVES ON THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF SODIUM-BOROSILICATE GLASSES

## L. G. Protasova<sup>1</sup> and V. G. Kosenko<sup>1</sup>

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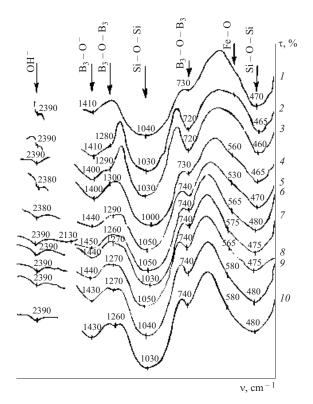
The structure of multicomponent sodium-borosilicate glasses is investigated using the IR spectroscopy method, and their physicochemical properties are identified. It is demonstrated that enamels for protecting pipes used in the oil sector can be obtained on the basis of these glasses.

The study in [1] investigated the water resistance of polycomponent glasses based on the  $\rm Na_2O\cdot B_2O_3\cdot SiO_2$  system with a constant ratio of the components (1:0.5:0.48) under a consecutive complication of the composition by introducing the additives FeO, Fe<sub>2</sub>O<sub>3</sub>, MnO, CaO, MgO, Li<sub>2</sub>O, CaF, Al<sub>2</sub>O<sub>3</sub>, CuO, and ZnO. It was demonstrated that water resistance does not always correlate with the quantity of sodium leached from the glass and can be determined by ionic exchange between sodium cations in the glass and hydrogen ions in the solution.

The present study analyzes the structure of the same glass compositions [1] using the IR spectroscopy method on a UR-20 spectrophotometer (a glass powder was compressed in KBr) and identifies the physicochemical properties of glasses: glass density using the hydrostatic weighing method and TCLE by the quartz dilatometry method.

The spectrum of initial composition 1 (Fig. 1) has absorption spectra at 470, 730, 1040, 1280, and 1410 cm<sup>-1</sup>, which represent, according to the data in [2], the deformation and stretching vibrations of bonds Si - O - Si,  $B_3 - O - B_3$ , Si - O - Si, and  $B_3 - O^-$ , and an absorption band at 2300 cm  $^{-1}$  reflecting the vibrations of OH $^{-}$  groups in the borate component. On introducing FeO, Fe<sub>2</sub>O<sub>3</sub>, and MnO, the bands become nearer to each other (Fig. 1, spectra 2 and 3), which is evidence of the incorporation of iron and manganese actions into the glass skeleton. On adding CaO, an additional band emerges at 560 cm<sup>-1</sup> (spectrum 4) characterizing the vibrations of the bond Fe - O, which is evidence of the localization of  $\mathrm{Fe^{2+}}$  cations near the  $\mathrm{BO_3}$  triangles, since the band at 1250 cm<sup>-1</sup> in this case shifts to 1300 cm<sup>-1</sup>. On replacing CaO by MgO and introducing other components into glass, no significant modifications are observed in the spectra, and insignificant shifts of the specified bands are due to a deformation of the glass skeleton.

Table 1 shows the physicochemical properties of glasses. It can be seen that the most significant density growth is observed in compositions 8 and 9 on introducing copper and zinc oxides, which may be related to their partial contributions: 6.46 and 5.70 g/cm³, respectively. Despite the fact that CaO and MgO play the same structural role of modifiers, the density of glass of 4 is higher than that of glass 5, which is also due to their partial contributions: 2.90 and 3.25 g/cm³, respectively. The molar volume of glasses decreases with in-



**Fig. 1.** IR transmission spectra of sodium-borosilicate glasses. Curve numbers correlate with glass compositions described in [1].

<sup>&</sup>lt;sup>1</sup> Ural State Technical University (UPI), Ekaterinburg, Russia.

creasing complexity of the composition, which points to the consolidation of the glass structure.

The softening point  $T_g$  and the deformation start temperature  $T_f$  were identified based on dilatometric expansion curves of the samples. These temperatures become lower as the composition becomes more complex, which agrees with the structural role of the modifier oxides introduced. Furthermore, glasses become "more short-termed" as the interval between the specified temperatures ( $\Delta T = T_f - T_g$ ) decreases from 50 to 20 K. Replacement of CaO by MgO leads to a perceptible increase in this interval: from 33 to 45 K.

Since the obtained compositions can serve as a basis for making enamels to protect pipes used in the oil sector, the TCLE of enamel should be coordinated with the TCLE of steel, which is equal to  $110\times10^{-7}\,\mathrm{K^{-1}}$  [3]. TCLEs of glasses calculated from the expansion curves are listed in Table 1. The minimum TCLE is registered in composition 4 with a CaO additive; accordingly, CaO was thereafter replaced by MgO. The majority of the compositions have the required values of TCLE.

Thus, as the compositions of sodium-borosilicate glasses become more complex, the temperatures of softening and start of glass deformation become lower, whereas the densities and TCLEs of glasses change nonlinearly and depend on the partial contributions of the components and their structural roles.

TABLE 1

Composi- tion	Density, g/cm <sup>3</sup>	Molar volume, cm³/mole	Temperature of, K		TCLE
			softening	deformation start	TCLE, 10 <sup>-7</sup> K <sup>-1</sup>
1	2.29	24.64	496	535	96
2	2.31	31.27	457	487	116
3	2.35	17.86	465	510	113
4	2.44	15.29	442	475	78
5	2.32	18.67	456	495	112
6	2.36	18.83	455	500	121
7	2.35	18.50	415	450	111
8	2.33	18.72	440	475	104
9	2.52	17.59	410	435	135
10	2.58	17.45	420	445	117

## **REFERENCES**

- P. I. Buler, L. G. Protasova, I. G. Kosnyreva, and E. V. Turaikina, "Resistance of multicomponent glasses to water," *Steklo Keram.*, No. 4, 9 – 10 (1990).
- 2. E. M. Milyukov, "Spectral absorption of liquating sodium-boro-silicate glasses tinted by iron oxides," *Prikl. Spektrosk.*, **32**(3), 516 518 (1980).
- 3. A. L. Appen, *Temperature-Resistant Inorganic Coatings* [in Russian], Khimiya, Leningrad (1976).